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# 川赤芍的化学成分研究*

李 鲜[1,2], 黎胜红[1], 普建新[1], 黄胜雄[1], 孙汉董[1**]
(1 中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室, 云南 昆明 650204;
2 昆明医学院药学院, 云南 昆明 650031)

**摘要**: 从川赤芍 *Paeonia anomala* subsp. *veitchii* 根皮的 70%丙酮提取物中, 分离鉴定了 22 个化合物, 其中包括一个新的 24, 30 位降常春藤皂苷三萜衍生物, 命名为 paeonenolide H (**1**)。化合物 **2, 4, 9, 10** 为首次从该植物中分离得到。

**关键词**: 芍药科; 川赤芍; 三萜化合物
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# Chemical Constituents from *Paeonia anomala* subsp. *veitchii* (Paeoniaceae)

LI Xian[1,2], LI Sheng-Hong[1], PU Jian-Xin[1], HUANG Sheng-Xiong[1], SUN Han-Dong[1**]
(1 *State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences*, Kunming 650204, China; 2 *College of Pharmacology, Kunming Medical College*, Kunming 650031, China)

**Abstract:** A new triterpenoid derivative, paeonenolide H (**1**) together with twenty-one known compounds, were isolated from the root cortex of *Paeonia anomala* subsp. *Veitchii* (Lynch). Their structures were elucidated on the basis of spectroscopic evidences. Compounds **2, 4, 9, 10** were isolated from this plant for the first time.

**Key words:** Paeoniaceae; *Paeonia anomala* subsp. *Veitchii*; Triterpenoids

*Paeonia anomala* subsp. *veitchii* (Lynch) (Hong *et al*. 2001) is one of the most important crude drugs in traditional Chinese medicine, used as antiinflammatory, analgesic and sedative agent. It is also frequently used as a remedy for female diseases (Wu, 1990). Phytochemical analysis on this plant led to isolation of twenty-two compounds (**1 - 22**), including a new triterpenoid derivative (**1**). In this paper, we describe the isolation and structural elucdation of **1**.

## Results and Discussions

Paeonenolide H (**1**), obtained as white amorphous powder, gave a quasimolecular ion peak at *m/z* 497 $[M-H]^-$ in the negative FABMS spectrum, corresponding to the molecular formula $C_{31}H_{46}O_5$ determined by the HR-FAB-MS. Considering the structures of triterpenoids previously isolated from the *P. anomala* subsp. *Veitchii* and careful inspection of the $^1$H- and $^{13}$C-NMR (including DEPT) spectra (Table 1), compound **1** should possess the skeleton of bisnortriterpenoid derivative similar to paeonenolide C (Wu *et al*. 2005). The prominent differences between two compounds were the presence of additional three carbon signals in **1** at $\delta_C$ 110.4 (s), 26.8 (q) and 26.5 (q), which were attributed to a 1, 3-dioxolane moiety. A careful analysis of the 2D NMR spectroscopic data led to the conclusion that the acetal C-atom of **1** was connected with C - 4 and C - 23 through O-atoms forming a five-membered 1, 3-dioxolane moiety instead of the six-membered 1, 3-dioxolane moiety of paeonenolide C, on the basis of

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** Author for correspondence. E-mail: hdsun@mail.kib.ac.cn, Tel: 0871 - 5223251
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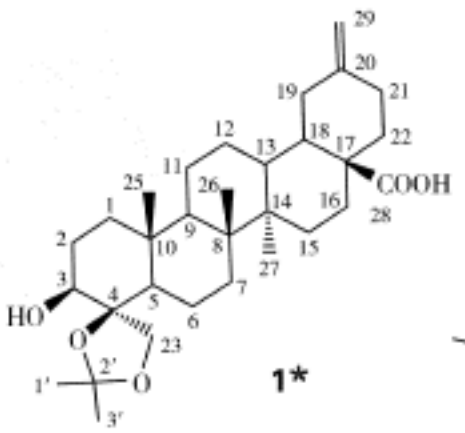
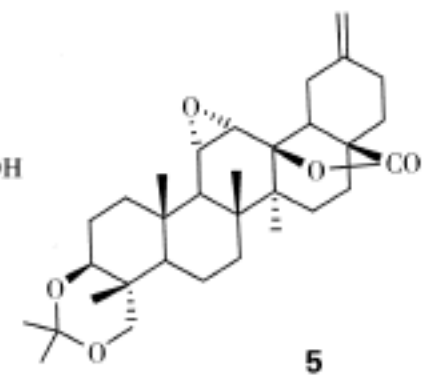
作者简介: 李鲜 (1974 - ) 女, 理学博士, 讲师, 主要从事植物化学研究。




**1***

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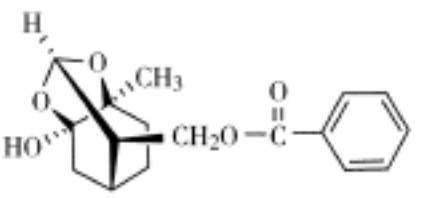


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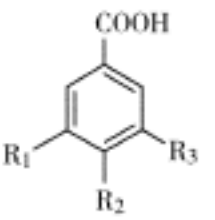
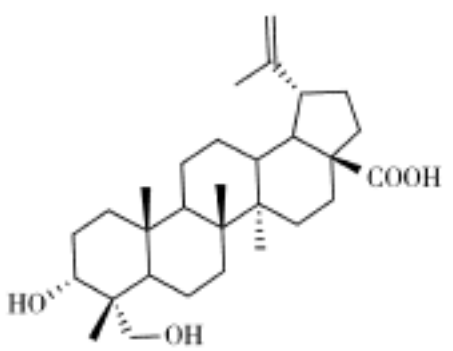



| | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| **13** | OH | OH | OH |
| **14** | H | H | H |

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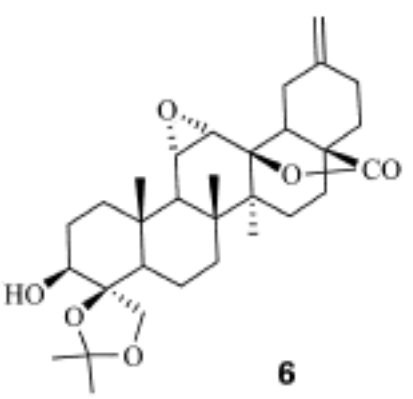


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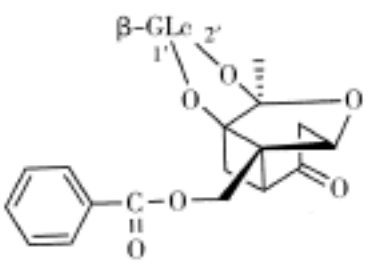


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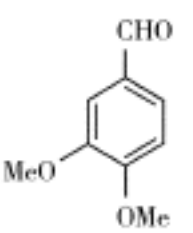


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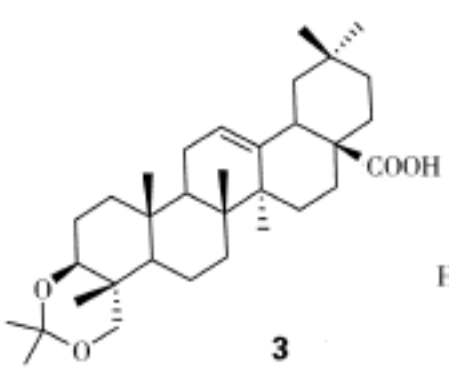


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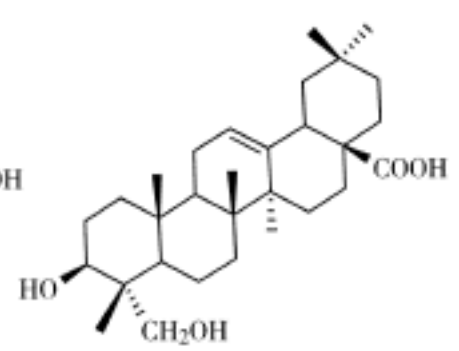


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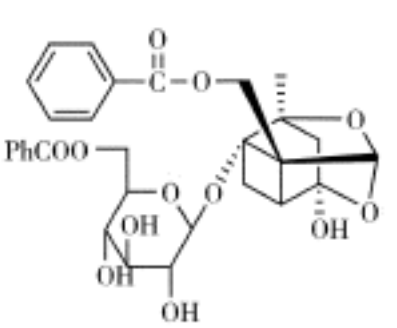


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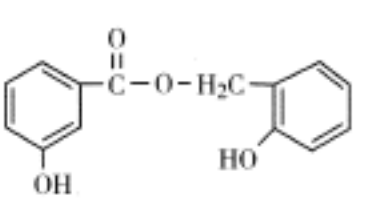


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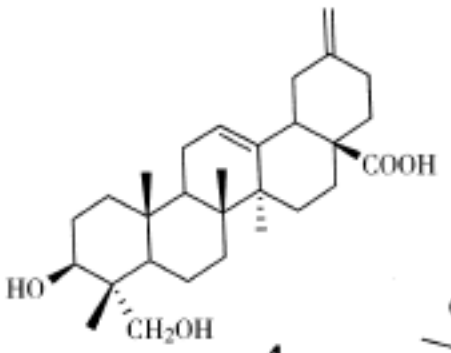


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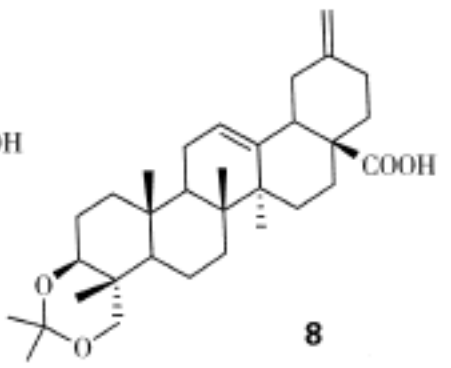


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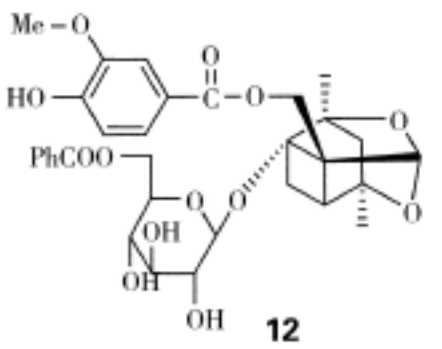


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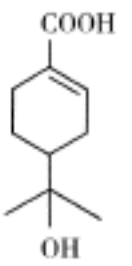


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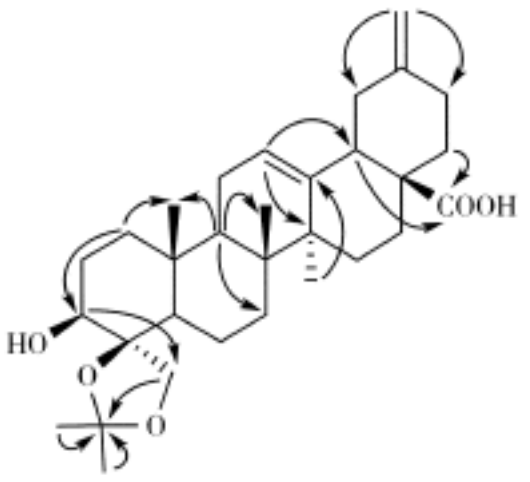


Fig . 1 The selected HMBC correlations of compound **1**

HMBC ( Fig . 1) correlations of H - 23 ($\delta_H$ 4.13 and 3.78, d, $J$ = 8.4 Hz, each 1H) and (Me)$_2$ C - 2′ ($\delta_H$ 1.40 and 1.36, s, each 3H) with the acetal C - 2′ atom ($\delta_C$ 110.4), and the absence of the HMBC correlation between H - 3 ($\delta_H$ 3.22, dd, $J$ = 5.0, 11.7 Hz, 1H) and the acetal C - 2′ atom . The abnormal downfield chemical shifts of the acetal C - 2′ atom and C - 4 were attributed to the strain effect in the five-membered ring . Thus, **1** was determined to be (3β, 4β) -3-hydroxy-4, 23 (isopropylidendioxy)-24, 30-dinorolean-12, 20 (29)-dien-28-oic acid .

The known compounds were determined as oplopanxogenin C (**2**) (Adam *et al* . 1982), 3β, 23-acetonide-hederagenin (**3**) (Wu *et al* . 2005), 3β, 4β, 23-trihydroxy-24, 30-dinor-olean-12, 20 (29)-dien-28-oic acid (**4**) (Wu *et al* . 2001), paeonenolide F (**5**) (Wu *et al* . 2005), paeonenolide G (**6**) (Wu *et al* . 2005), hederagenin (**7**) (Ikuta and Itokawa,

1988), 3β, 23-acetonide-4β-hydroxy-24, 30-dinorolean-12, 20 (29)-dien-28-oic acid (**8**) (Wu *et al* . 2005), paeoniflorigenone (**9**) (Shimizu *et al* . 1981), lactiflorin (**10**) (Lang *et al* . 1990), benzoylpaeoniflorin (**11**) (Ishida *et al* . 1987), 6′-O-benzoyl-4″-hydroxy-3″-methoxy-paeoniflorin (**12**) (Wu *et al* . 2002), gallic acid (**13**), benzoic acid (**14**), 3, 4-dimethoxybenzaldehyde (**15**), 2-hydroxy-benzyl-3-hydroxy-benzoate (**16**), euglobal (**17**) (Kozuka *et al* . 1982), twenty-two carboxylic acid (**18**), 2-hydroxy-1-linoleic acid-propaneyl ester (**19**), 2-hydroxy-1-linolenic acid-propaneyl ester (**20**), daucosterol (**21**), β-sitosterol (**22**) .

## Experimental Part

**General** Optical rotation was recorded on a SEPA-300 polarimetre . UV spectrum was obtained on a Shimadzu double-beam 210A spectrometer in pyridine . The MS spectra were performed on a VG Autospec-3000 spectrometer with 70 eV . $^{1}$H, $^{13}$C NMR and 2D NMR were recorded on a Bruker AM-400 and DRX-500 spectrometer with TMS as internal standard . The silica gel for TLC and column chromatography were obtained from Qingdao Marine Chemical Inc ., China .

**Plant Material** The root cortex of *Paeonia anomala* subsp. *Veitchii* was bought from Crude Drug Company, in Kunming, Yunnan Province, in December 2003 . It was identified by Professor Lin Zhong-Wen . The voucher specimen (KIB-2003-024 Lin) was deposited in Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences .

**Extraction and Isolation** The dried and powdered root cortex (14.5 kg) were extracted with 70% acetone at room temperature for 3 × 24 h . The extract was concentrated and partitioned between EtOAc and $H_2O$ . The EtOAc extract (1.14 kg) was subjected to column chromatography over silica gel (100-200 mesh, 2.5 kg) eluting with $CHCl_3$/$Me_2CO$ (from 1∶0 to 0∶1) to give six fractions . Compounds **13** (1.05 g), **14** (15.0 g) **15** (12 mg), **16** (15 mg), **19** (15 mg), **22** (60 mg) were obtained from fraction Ⅰ, **2** (15 mg), **4** (12 mg) were purified from fraction Ⅱ, **9** (1.50 g), **20** (19 mg) were purified from fraction Ⅲ, **3** (2 mg), **7** (15 mg), **8** (20 mg), **5** (11 mg), **1** (6 mg), **6** (8 mg), **17** (75 mg) were achieved from fraction Ⅳ, and **21** (15 mg), **12** (105 mg), **11** (25 mg), **10** (25 mg), **18** (8 mg) were achieved from fraction Ⅴ, respectively, after repeatedly RP-18 and Sephadex LH-20 column chromatography and semipreparative reverse-phase HPLC .

**Paeonenolide H (1):** white needles crystal; $C_{31}H_{46}O_5$; $[\alpha]_D^{21}$ + 92.4° (*c* 1.46, $C_5H_5N$) . UV $\lambda_{max}^{MeOH}$ nm: 203 (3.98); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3432, 2936, 1721, 1697, 1459, 1378, 1194; FAB (negative) *m*/*z*: 497 $[M-H]^-$; HR-FABMS (negative): 497.3254 (calcd . for $C_{31}H_{46}O_5$: 497.3267); $^{1}$H and $^{13}$C NMR (pyridine-$d_5$) data see Table 1 .

**Oplopanaxogenin C (2):** white amorphous powder; $C_{30}H_{48}O_4$; Mp . 270-273℃; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3426, 2942, 1692, 1640, 1452, 1384, 1046; $[\alpha]_D^{20}$ + 8° (*c* 0.4, $CHCl_3$) . NMR data: same as the data reported in Adam *et al* . (1982) .

**3β, 23-acetonide Hederagenin (3):** white amorphous powder; $C_{30}H_{48}O_4$; EIMS *m*/*z*: 498 $[M]^+$, 265, 248 (100), 203 . NMR data: same as the data reported in Wu *et al* . (2005) .

**3β, 4β, 23-trihydroxy-24, 30-dinorolean-12, 20 (29)-dien-28-oic acid (4):** white amorphous powder; $C_{28}H_{42}O_4$; $[\alpha]_D^{24}$ + 89.3° (*c* 0.252, MeOH) . UV $\lambda_{max}^{MeOH}$ nm: 204.5; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3421, 2936, 1719, 1690, 1663, 1465, 1443, 1382, 1295, 1046, 886 . NMR data: same as the data reported in Wu *et al* . (2001) .

Table 1　$^{1}$H and $^{13}$C NMR data of compound **1** (in pyridine-$d_5$, *J* in Hz)

| No . | $\delta_H$ | $\delta_C$ | No . | $\delta_H$ | $\delta_C$ |
|---|---|---|---|---|---|
| 1 | 1.38 (1H, m), 0.84 (1H, overlap) | 38.2 (t) | 17 | | 46.8 (s) |
| 2 | 1.66 (2H, overlap) | 27.6 (t) | 18 | 2.71 (1H, dd, 4.7, 10.8) | 46.9 (d) |
| 3 | 3.22 (1H, dd, 5.0, 11.7) | 71.1 (d) | 19 | 2.50 (1H, t like, 10.8), 2.15 (1H, overlap) | 41.2 (t) |
| 4 | | 85.3 (s) | 20 | | 147.8 (s) |
| 5 | 0.84 (1H, overlap) | 52.8 (d) | 21 | 2.10 (1H, overlap), 2.15 (1H, overlap) | 30.0 (t) |
| 6 | 1.61 (2H, m) | 19.2 (t) | 22 | 1.89 (2H, m) | 37.3 (t) |
| 7 | 1.43 (1H, m), 1.12 (1H, m) | 32.3 (t) | 23 | 4.13 (1H, d, 8.4), 3.78 (1H, d, 8.4) | 70.0 (t) |
| 8 | | 39.4 (s) | 25 | 0.99 (3H, s, Me-25) | 14.7 (q) |
| 9 | 1.52 (1H, dd, 7.4, 10.8) | 46.5 (d) | 26 | 0.80 (3H, s, Me-26) | 17.0 (q) |
| 10 | | 37.4 (s) | 27 | 1.15 (3H, s, Me-26) | 25.9 (q) |
| 11 | 1.76 (1H, overlap) | 23.1 (t) | 28 | | 182.4 (s) |
| 12 | 5.35 (1H, d, 3.2) | 123.2 (d) | 29 | 4.62 (2H, br s) | 107.1 (t) |
| 13 | | 142.9 (s) | C-2′ | | 110.4 (s) |
| 14 | | 42.1 (s) | Me-1′ | 1.40 (3H, s) | 26.8 (q) |
| 15 | 2.10 (1H, overlap), 1.76 (1H, overlap) | 28.4 (t) | Me-3′ | 1.36 (3H, s) | 26.5 (q) |
| 16 | 2.10 (1H, overlap), 1.66 (1H, overlap) | 23.3 (t) | | | |

**Paeonenolide F (5) :** white amorphous powder; $C_{32}H_{46}O_5$; $[\alpha]_D^{24}$ + 71.1°(*c* 0.24, $CHCl_3$); UV $\lambda_{max}^{MeOH}$ nm: no absorption; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 2938, 2859, 1777, 1466, 1391, 1361, 1256, 1220, 1167, 1133, 1114, 1067, 1024, 932, 895, 872, 863; EIMS *m/z*: 510 $[M]^+$, 495 (100), 435, 291, 263, 247, 233, 219, 201, 189, 173, 159, 147, 119, 105, 95. NMR data: same as the data reported in Wu *et al*. (2005).

**Paeonenolide G (6) :** white amorphous powder; $C_{32}H_{46}O_5$; $[\alpha]_D^{24}$ + 92.1°(*c* 0.35, $CHCl_3$); UV $\lambda_{max}^{MeOH}$ nm: no absorption; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3528, 3063, 2946, 1775, 1647, 1396, 1365, 1257, 1230, 1146, 1079, 1051, 985, 927, 873; EIMS *m/z*: 512 $[M]^+$, 497 (100), 468, 453, 437, 293, 265, 247, 232, 221, 203, 189, 173, 159, 147, 105, 91. NMR data: same as the data reported in Wu *et al*. (2005).

**Hederagenin (7) :** white amorphous powder; $C_{30}H_{48}O_4$; UV $\lambda_{max}^{MeOH}$ nm: 206 (3.78); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3449, 2943, 2577, 1697, 1463, 1386, 1267, 1206, 1037, 1013, 653; EIMS *m/z*: 472 $[M]^+$, 454, 426, 248 (100), 223, 203, 187, 175, 119, 107, 95, 81, 69. NMR data: same as the data reported in Ikuta *et al*. (1988).

**3β, 23-acetonide-4β-hydroxy-24, 30-dinorolean-12, 20 (29)-dien-28-oic acid (8) :** $C_{32}H_{48}O_4$; FABMS (negative) *m/z*: 495 $[M-H]^-$. NMR data: same as the data reported in Wu *et al*. (2005).

**Paeoniflorigenone (9) :** $C_{17}H_{18}O_6$; UV $\lambda_{max}^{MeOH}$ nm: 240.5, 274.5, 282.0; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3421, 2971, 1723, 1600, 1451, 1397, 1315, 1278, 1102, 1171, 1033, 963, 712. NMR data: same as the data reported in Shimizu *et al*. (1981).

**Lactiflorin (10) :** white amorphous powder; $C_{23}H_{26}O_{10}$; Mp. 195 - 198℃; $[\alpha]_D^{23}$ + 37.2°(*c* 0.90, EtOH); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3505 - 3460, 1745, 1722, 1450, 1380, 1340, 1275, 1230, 1174, 1110, 1065, 1025, 968, 892, 850; EIMS *m/z*: 462 $[M]^+$, 371, 340, 300, 285 (100), 255, 214, 196, 178, 163, 162, 150, 135, 127, 122, 105, 77. NMR data: same as the data reported in Lang *et al*. (1990).

**Benzoylpaeoniflorin (11) :** white amorphous powder; $C_{30}H_{32}O_{12}$; $[\alpha]_D^{17}$ = - 13.97°(*c* = 0.36, MeOH); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3450, 2904, 1713, 1600, 1554, 1452, 1345, 1278, 1177, 1070, 956, 712. NMR data: same as the data reported in Ishida *et al*. (1987).

**6′-O-benzoyl-4′-hydroxy-3′-methoxy-aeoniflorin (12) :** white amorphous powder; $C_{31}H_{34}O_{14}$; $[\alpha]_D^{17}$ - 13.95°(*c* 0.43, MeOH); UV $\lambda_{max}^{MeOH}$ nm: 203 (4.36); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3430, 1711, 1599, 1514, 1450, 1428, 1383, 1345, 1284, 1222, 1179, 1115, 1073, 1025, 823, 763, 714. NMR data: same as the data reported in Wu *et al*. (2002).

**Gallic acid (13) :** colorless needle; $C_7H_6O_5$; Mp. 247 - 249℃; UV $\lambda_{max}^{MeOH}$ nm: 270; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3490, 3060, 2650, 1708, 1623, 1524, 1450, 1330, 1246, 1031, 954; FABMS (negative) *m/z*: 169 $[M-H]^-$.

**Benzoic acid (14) :** colorless needle; $C_7H_6O_5$; EIMS *m/z*: 122 $[M]^+$, 105 (100), 94, 77, 58. The value of $R_f$ is consistent with that of authentic sample on TLC.

**3, 4-dimethoxybenzaldehyde (15) :** colorless needle; $C_9H_{10}O_3$; FABMS (negative) *m/z*: 165 $[M-H]^-$. NMR data: same as the data reported in Aldrich Library of $^{13}C$ and $^1H$ NMR spectra.

**2-hydroxy-benzyl-3-hydroxy-benzoate (16):** yellow amorphous powder; $C_{14}H_{12}O_4$; FABMS (negative) *m/z*: 243 $[M-H]^-$.

**Euglobal (17) :** colorless needle; $C_{10}H_{16}O_3$; ESIMS (negative) *m/z*: 183 $[M+H]^+$. NMR data: same as the data reported in Kozuka *et al*. (1982).

**Twenty-two carboxylic acid (18) :** $C_{23}H_{46}O_2$; FABMS (negative) *m/z*: 339 $[M-H]^-$.

**2-hydroxy-1-linoleic acid-propaneyl ester (19) :** $C_{21}H_{38}O_4$; FABMS (positive) *m/z*: 355 $[M+H]^+$.

**2-hydroxy-1-linolenic acid-propaneyl ester (20) :** $C_{21}H_{36}O_4$; FABMS (positive) *m/z*: 353 $[M+H]^+$.

**Daucosterol (21) :** FAB MS *m/z* 575 ($[M-1]^-$); The value of $R_f$ is consistent with that of authentic sample on TLC.

**β-Sitosterol (22) :** EI MS *m/z* 414 ($[M]^+$, 80); The value of Rf is consistent with that of authentic sample on TLC.

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